

# PATENT SPECIFICATION

(11) 1281 112

1281 112

NO DRAWINGS

(21) Application No. 10769/70 (22) Filed 6 March 1970

(45) Complete Specification published 12 July 1972

(51) International Classification B01J 11/32

(52) Index at acceptance

B1E 20Y 23X 271 275 277 300 303 304 330 33Y 341  
342 343 34Y 350 35Y 361 36Y 390 39Y 400 40Y  
420 422 42Y 43X 43Y 471 47Y 510 514 515 520  
522 535 551 55Y 570 690 691

C5E D3



## (54) A METHOD OF PREPARING CATALYSTS

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The present invention relates to a method of preparing catalysts consisting of metal oxides, used in oxidation-reduction reactions, for example in the conversion of carbon monoxide with steam, or in hydrogenation or dehydrogenation processes.

A known method of preparing the above catalysts consists in the coprecipitation of the oxides of magnesium, aluminium and also of metals located in the periodic table of elements with increasing atomic weight from calcium to gallium and from strontium to polonium, by mixing dilute 10 to 20% by weight aqueous solutions of nitrate and/or acetate salts of the above metals with a second component—the hydroxides or carbonates of alkali metals and ammonia, followed by separating the precipitate, washing it free of soluble salts, drying, calcining at a temperature of from 300° to 700°C. and molding (see for example British Patent Specification No. 1,082,297; Belgian Patent Specification Nos. 683,059 and 689,977; and Dutch Patent

Specifications Nos. 6,414,056 and 6,601,536).

This known method has a number of disadvantages, the most serious of which are the following:

- 1) The difficulty of washing the precipitate free of soluble salts, whose presence (particularly that of alkali metal salts) in the catalyst even in very small quantities (more than 0.2% by weight) markedly decreases the activity of the latter;
- 2) The formation of a large quantity of contaminated water and the necessity for utilizing it;
- 3) The complexity of the technological process for preparing the catalysts; and
- 4) The complexity of the process equipment.

The object of the present invention is to obviate or mitigate the above disadvantages.

According to the present invention there is provided a method of preparing a non-supported catalyst suitable for use in oxidation-reduction reactions, said method comprising providing an aqueous solution or melt of a first component selected from the nitrate and acetate salts of the elements selected from magnesium, aluminium and those of atomic number from 20 to 31 and from 38 to 84, said aqueous solution, if used, having a total salt concentration of from 35 to 80% by weight; obtaining a precursor mass by mixing with the aqueous solution or melt a second component comprising oxalic acid or a powdered compound selected from the carbonates, basic carbonates and hydroxides of the elements selected from magnesium, aluminium and those of atomic number from 20 to 31 and from 38 to 84; and, in the absence of a separate catalyst support, calcining the precursor mass at a temperature within the range from 300 to 700°C.

In order to decrease the cost of the catalysts, up to 99.9% of the expensive chromium nitrate calculated as  $\text{Cr}_2\text{O}_3$  may be substituted by chromic anhydride if chromium is to be

the or one of the selected metal(s); this is effected by adding powdered chromic anhydride to a concentrated (35 to 80%, by weight) aqueous solution or melt of chromium nitrate before mixing with the second component.

In order to obtain a uniform paste-like precursor mass which leads to improving the properties of the catalysts, vigorous mixing at a temperature of from 70 to 100° is recommended, after the mixing of the components of the precursor mass and before calcination.

By virtue of the present invention it is possible to prepare a catalyst by a method which has the following advantages over known methods:

1. There is eliminated the laborious operation of separating the precipitate and washing the latter free of soluble salts;
2. There is excluded the possibility of the slightest contamination of the catalyst with alkali metals, thus providing a constant high activity of the catalysts obtained;
3. The operation of drying a precursor mass before calcination is unnecessary;
4. The formation of waste water is reduced; and
5. The process equipment is simplified.

The present invention also provides a catalyst when made by the method of the present invention, and, in a preferred embodiment, a catalyst for the steam conversion of carbon monoxide.

Known catalysts for the conversion of carbon monoxide with steam consist of from 5 to 80%, by weight of copper oxide, from 3 to 40%, by weight of chromium oxide, from 3 to 80%, by weight of aluminium oxide and from 1 to 30%, by weight of magnesium oxide or zinc oxide (see for example Belgian Patent Specification No. 719,214 and French Patent Specification No. 1,578,433).

The above known catalysts have the following disadvantages:

1. Low thermal stability (the catalyst considerably lowers its activity on overheating in the reaction medium at temperatures above 400°C);
2. Low mechanical strength; and
3. High bulk density of the catalyst (from 1.6 to 1.8 kg/l for tablets of height 5 mm and diameter 5 mm).

By the present method there are obtainable catalysts suitable for the conversion of carbon monoxide with steam, which consist of the above components but with a different proportion between these components in weight percent, namely: CuO— from 30 to 55%, MgO— from 25 to 45%, Al<sub>2</sub>O<sub>3</sub>— from 2 to 30%, Cr<sub>2</sub>O<sub>3</sub> or ZnO— from 0 to 30%.

The above catalysts exhibit the following advantages in comparison with the known catalysts:

- 1) High activity (the process of the conversion of carbon monoxide with steam takes place with catalysts of this invention at a starting temperature of from 180 to 120°C, and at a temperature of from 180 to 200°C there is provided a residual carbon monoxide content which is close to the equilibrium value);
- 2) The mechanical strength on crushing catalyst tablets of diameter 5 mm and height 5 mm is not less than 280 kg/cm<sup>2</sup>;
- 3) Increased thermal stability (the catalysts retain their activity on overheating in the reaction medium up to 500°C); and
- 4) Low bulk density of the catalysts (no greater than 1.3 kg/l for tablets of height 5 mm and diameter 5 mm).

An embodiment of a method of preparing catalysts suitable for use in oxidation-reduction reactions is effected in the following way.

There is prepared a 35 to 80% by weight concentrated aqueous solution of the nitrate salt(s) of magnesium, aluminium and or other metal(s) located in the periodic table of elements in the range from calcium to gallium and from strontium to polonium with increasing atomic weight, by dissolving the salt(s) in water at a temperature of from 60 to 80°C or by dissolving the corresponding metal(s), or the oxide(s), hydroxide(s) and/or carbonate(s) thereof, in a concentrated or dilute aqueous solution of nitric acid. (Where the aqueous solution of nitric acid has a concentration of less than 30%, by weight the aqueous solution of the metal nitrate(s) obtained is adjusted to the required concentration by evaporation).

The preparation of a 35 to 80% by weight concentrated aqueous solution of acetate salt(s) of the above metal(s) is effected by effecting solution of the salt(s) in water at a temperature of from 60 to 80°C.

The preparation of a melt of nitrate and/or acetate salt(s) of the above metal(s) is effected by heating the salt(s) to a temperature of from 70 to 90°C with stirring.

The prepared concentrated aqueous solution of nitrate and/or acetate salt(s) of the metal(s) or the melt is mixed with a powdered carbonate and/or a powdered basic carbonate and/or a powdered hydroxide of any of the aforesaid metals, and/or with oxalic acid.

To obtain a uniform paste-like precursor mass, the mixture is stirred vigorously at a temperature of from 70 to 100°C in a special mixer designed for the working of pastes. The stirring is continued until there is obtained a uniform paste which contains from 25 to 35%, by weight of residual moisture.

The calcination of the precursor mass is

then effected at a temperature within the range from 300 to 700°C and is then moulded, for example into granules or tablets, with or without the addition of a binding material or a lubricant. Preferred binding materials are kaolin and cement, although others may be used and preferred lubricants are graphite and talc.

For a better understanding of the present invention there are given the following examples of the preparation of the catalysts, intended for use in oxidation-reduction reactions.

#### EXAMPLE 1

A mixture of 112.5 g  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ , 40 g  $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  and 147.5 g  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$  was dissolved at 70°C in 140 g water. To the concentrated solution obtained, with constant stirring, there were added 108.2 g of powdered basic magnesium carbonate, after which the mixture was vigorously stirred in a mixer at 90°C for a period of 2 hours. The precursor mass obtained was thereafter calcined at a temperature of 550°C until all the nitrogen oxides were removed and the catalyst was ground, mixed with 2 g graphite and tabletted.

There were obtained 107.1 g catalyst (not taking into account the graphite) with the following composition (weight %):  $\text{Al}_2\text{O}_3$  14.3,  $\text{Cr}_2\text{O}_3$  7.1;  $\text{CuO}$  37.2;  $\text{MgO}$  41.4.

The catalyst was tested for activity in the process of the conversion of carbon monoxide in a gas of the following composition in volume percent:  $\text{CO}$ —25.3;  $\text{H}_2$ —65.0;  $\text{N}_2$ —18.7. The testing was carried out in a laboratory continuous flow set-up at atmospheric pressure at a space velocity of the dry reagent gas of 2000  $\text{hr}^{-1}$  and with a volume ratio of steam to reagent gas of 1:1. The catalyst was preliminarily reduced with the working gas (steam-gas mixture) at a temperature of 300°C.

In order to test the catalyst, simultaneously for activity and thermal stability, the conversion process was carried out first at a rising temperature of from 300 to 500°C and then at a falling temperature of from 500 to 200°C.

For testing there were taken 3  $\text{cm}^3$  of catalyst of the above composition with a granule size of from 1.5 to 2.5 mm.

The results of the testing are given in Table I.

TABLE I

| Temperature<br>°C | Residual content of<br>carbon monoxide in<br>the converted gas<br>Volume % |
|-------------------|--|
|                   |  |
| 300               | 1.10   |
| 500               | 3.40   |
| 300               | 1.00   |
| 200               | 0.35   |

#### EXAMPLE 2

The process was carried out as described

in Example 1, the only difference being that instead of 112.5 g  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ , there were taken 56.3 g  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ , and 23.4 g powdered aluminium hydroxide were added to 108.2 g powdered basic magnesium carbonate.

There was obtained a catalyst, whose composition was as given in Example 1.

The catalyst was tested in the process of the conversion of carbon monoxide in a gas whose composition, given in volume per cent was:  $\text{CO}$ —21.3;  $\text{H}_2$ —59.0;  $\text{N}_2$ —19.7. All the other conditions of the testing were analogous to those of Example 1.

The results of the testing are given in Table II.

TABLE II

| Temperature<br>°C | Residual content of<br>carbon monoxide in<br>the converted gas<br>Volume % |
|-------------------|--|
|                   |  |
| 300               | 0.80   |
| 500               | 3.45   |
| 300               | 0.90   |
| 200               | 0.30   |

#### EXAMPLE 3

A mixture of 30 g  $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ , 15 g  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  and 148.5 g  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$  was dissolved at 70°C in 140 g water. To the concentrated solution obtained there was added with constant stirring a mixture of 12.6 g of powdered zinc carbonate with 53.4 g of powdered basic magnesium carbonate. Then, the precursor mass obtained was mixed and calcined and the catalyst tabletted as described in Example 1.

There were obtained 80.2 g catalyst (without taking into account the graphite) of the following composition in weight %:  $\text{ZnO}$ —20.4;  $\text{Al}_2\text{O}_3$ —2.6;  $\text{CuO}$ —50.0;  $\text{MgO}$ —27.0.

The catalyst was tested in the conversion of carbon monoxide under conditions analogous to those of Example 2.

The testing results are given in Table III.

TABLE III

| Temperature<br>°C | Residual carbon monoxide<br>content in the con-<br>verted gas, volume % |
|-------------------|---|
|                   |   |
| 300               | 0.80  |
| 400               | 2.75  |
| 500               | 3.55  |
| 300               | 0.80  |
| 200               | 0.35  |

#### EXAMPLE 4

A mixture of 158.1 g  $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ , 73.5 g  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  and 60.4 g  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$  was dissolved at a temperature of 90°C in 70 g water. To the concentrated solution obtained there was added with a constant stirring a mixture of 28 g of

powdered basic copper carbonate and 87 g of powdered basic magnesium carbonate. The precursor mass obtained was then vigorously stirred and calcined and the catalyst tabletted as described in Example 1.

There were obtained 115.5 g catalyst (without taking into account the graphite) of the following composition in weight %: CuO—34.6, Cr<sub>2</sub>O<sub>3</sub>—26.0, Al<sub>2</sub>O<sub>3</sub>—8.7, MgO—30.7.

The catalyst was tested in the conversion of carbon monoxide under conditions analogous to those of Example 2.

The testing results are given in Table IV.

TABLE IV  
Residual carbon monoxide content in the converted gas, Volume %

| Temperature °C | Residual carbon monoxide content in the converted gas, Volume % |
|----------------|---|
| 300            | 1.15  |
| 500            | 3.45  |
| 20 300         | 1.17  |
| 200            | 0.40  |

#### EXAMPLE 5

A mixture of 112.5 g Al(NO<sub>3</sub>)<sub>3</sub> · 9 H<sub>2</sub>O, 40 g Cr(NO<sub>3</sub>)<sub>3</sub> · 9 H<sub>2</sub>O and 136 g Cu(NO<sub>3</sub>)<sub>2</sub> · 6 H<sub>2</sub>O was melted at a temperature of 90°C. To the melt obtained there were added with thorough stirring 171 g of powdered manganese carbonate. Then the precursor mass was vigorously stirred in a mixer at a temperature of 100°C for three hours and calcined at a temperature of 500°C; the catalyst was ground, mixed with 4.4 g graphite and tabletted.

There were obtained 220 g catalyst (without taking into account the graphite) of the following composition in weight %: Al<sub>2</sub>O<sub>3</sub>—11.8; Cr<sub>2</sub>O<sub>3</sub>—5.9; CuO—30.8; MnO—51.5.

The catalyst was tested in the conversion of carbon monoxide under conditions analogous to those of Example 2.

The results of the testing are given in Table V.

TABLE V  
Residual carbon monoxide content in the converted gas, Volume %

| Temperature °C | Residual carbon monoxide content in the converted gas, Volume % |
|----------------|---|
| 300            | 0.8   |
| 500            | 3.2   |
| 300            | 0.7   |
| 50 200         | 0.7   |

#### EXAMPLE 6

A mixture of 43.6 g Zn(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> · 2 H<sub>2</sub>O, 59 g Zn(NO<sub>3</sub>)<sub>2</sub> · 6 H<sub>2</sub>O, 177.8 g Al(NO<sub>3</sub>)<sub>3</sub> · 9 H<sub>2</sub>O and 134 g Cu(NO<sub>3</sub>)<sub>2</sub> · 3 H<sub>2</sub>O was dissolved at a temperature of 70°C in 180 ml water. To the concentrated solution obtained there were added with constant stirring 220 g of powdered oxalic acid, after which the mass obtained was vigorously stirred in a special mixer at a temperature of 90°C for 2 hours. The precursor mass obtained was

calcined at a temperature of 500°C, and the catalyst was ground, mixed with 2 g graphite and tabletted.

There were obtained 100 g catalyst (without taking into account the graphite) of the following composition in weight %: ZnO—32.0%, Al<sub>2</sub>O<sub>3</sub>—24.1%, CuO—43.9%.

The catalyst was tested under conditions analogous to those of Example 2 with the exception that the conversion of carbon monoxide was carried out first at rising temperature from 200 to 400°C and then at falling temperature from 400 to 180°C.

The results of the testing are given in Table VI.

TABLE VI  
Residual carbon monoxide content in the converted gas, Volume %

| Temperature °C | Residual carbon monoxide content in the converted gas, Volume % |
|----------------|---|
| 200            | 0.40  |
| 400            | 2.20  |
| 200            | 0.25  |
| 180            | 0.40  |

#### EXAMPLE 7

A mixture of 104.2 g Zn(NO<sub>3</sub>)<sub>2</sub> · 6 H<sub>2</sub>O, 158 g Al(NO<sub>3</sub>)<sub>3</sub> · 9 H<sub>2</sub>O, 119 g Cu(NO<sub>3</sub>)<sub>2</sub> · 3 H<sub>2</sub>O and 56.4 g Cr(NO<sub>3</sub>)<sub>3</sub> · 9 H<sub>2</sub>O was fused at a temperature of 90°C. To the melt obtained there were added with thorough stirring 230 g powdered oxalic acid, after which the precursor mass was worked up as described in Example 6.

There were obtained 100 g catalyst (without taking into account the graphite) of the following composition in weight %: ZnO—28.6, Al<sub>2</sub>O<sub>3</sub>—21.5, CuO—39.2, Cr<sub>2</sub>O<sub>3</sub>—10.7.

The catalyst was tested under conditions analogous to those of Example 2 with the exception that the temperature cycle of the conversion of carbon monoxide is that shown in Table VII.

TABLE VII  
Residual carbon monoxide content in the converted gas, Volume %

| Temperature °C | Residual carbon monoxide content in the converted gas, Volume % |
|----------------|---|
| 200            | 0.3   |
| 400            | 2.4   |
| 200            | 0.4   |

#### EXAMPLE 8

A mixture of 162.1 g Al(NO<sub>3</sub>)<sub>3</sub> · 9 H<sub>2</sub>O, 57.8 g Cr(NO<sub>3</sub>)<sub>3</sub> · 9 H<sub>2</sub>O, 178 g Cu(NO<sub>3</sub>)<sub>2</sub> · 3 H<sub>2</sub>O and 57.8 g Mg(NO<sub>3</sub>)<sub>2</sub> · 6 H<sub>2</sub>O was melted at 90°C with constant stirring. To the melt obtained there were added 250 g powdered oxalic acid, after which the precursor mass was vigorously stirred and calcined and the catalyst obtained tabletted as described in Example 6.

There were obtained 100 g catalyst (without taking into account the graphite) of the following composition in weight %: Al<sub>2</sub>O<sub>3</sub>—22, Cr<sub>2</sub>O<sub>3</sub>—11, CuO—58, MgO—9.

The catalyst was tested in the conversion of carbon monoxide under conditions analogous to those of Example 7.

The results of the testing are given in Table VIII.

TABLE VIII  
Residual carbon monoxide  
content in the con-  
verted gas, Volume %

| Temperature<br>°C | Residual carbon monoxide<br>content in the con-<br>verted gas, Volume % |
|-------------------|---|
| 200               | 0.3   |
| 400               | 2.3   |
| 200               | 0.3   |

#### EXAMPLE 9

A mixture of 63.5 g  $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ , 32.4 g  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  and 145 g  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$  was melted at a temperature of 90°C with constant stirring. To the melt obtained there were added 21.1 g powdered basic magnesium carbonate, 33.6 g powdered aluminium hydroxide and 118.6 g powdered oxalic acid. Then the precursor mass was vigorously mixed and calcined and the catalyst obtained was tabletted as described in Example 6.

There were obtained 100 g catalyst (without taking into account the graphite) of the following composition weight %:  $\text{ZnO}$ —17.4,  $\text{MgO}$ —8.7,  $\text{Al}_2\text{O}_3$ —26.2,  $\text{CuO}$ —47.7.

The catalyst was tested in the conversion of carbon monoxide under conditions analogous to those of Example 6.

The results of the testing are given in Table IX.

TABLE IX  
Residual carbon monoxide  
content in the con-  
verted gas, Volume %

| Temperature<br>°C | Residual carbon monoxide<br>content in the con-<br>verted gas, Volume % |
|-------------------|---|
| 200               | 0.3   |
| 400               | 2.1   |
| 200               | 0.2   |
| 180               | 0.3   |

#### EXAMPLE 10

A mixture of 3.9 kg  $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ , 60.4 kg  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$  and 37 kg  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  was melted at a temperature of 90°C. To the melt obtained there were added 5.8 kg powdered chromic anhydride, and then 49 kg powdered basic magnesium carbonate. Then the precursor mass was vigorously stirred in a mixer at 90°C for 3 hours after which it was calcined at 600°C and stirred for 8 hours; the catalyst obtained was ground and mixed with 1 kg graphite and tabletted.

There were obtained 50 kg catalyst (without taking into account the graphite) of the following composition in weight %:  $\text{MgO}$ —40,  $\text{CuO}$ —40,  $\text{Al}_2\text{O}_3$ —10,  $\text{Cr}_2\text{O}_3$ —10.

The catalyst was tested in the conversion of carbon monoxide under conditions analogous to those of Example 2.

The results are given in Table X.

TABLE X  
Residual carbon monoxide  
content in the con-  
verted gas, Volume %

| Temperature<br>°C | Residual carbon monoxide<br>content in the con-<br>verted gas, Volume % |    |
|-------------------|---|----|
| 300               | 0.5   | 65 |
| 500               | 3.8   |    |
| 300               | 0.4   |    |
| 200               | 0.3   |    |

#### EXAMPLE 11

A mixture of 145.6 g  $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ , 75.3 g  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  and 52.4 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  was melted at a temperature of 90°C with stirring. To the melt obtained there was added at 100°C with constant stirring a mixture of 15.7 g powdered aluminium hydroxide and 75.5 g basic magnesium carbonate. The paste-like mass obtained was calcined at 550°C for 5 hours and the catalyst obtained was ground, mixed with 2 g graphite and tabletted.

There were obtained 100 g catalyst (without taking into account the graphite) of the following composition (weight %):  $\text{Ni}_2\text{O}_3$ —40,  $\text{Al}_2\text{O}_3$ —20,  $\text{MgO}$ —30,  $\text{Fe}_2\text{O}_3$ —10.

The catalyst was tested in the preparation of high purity hydrogen by the removal of the carbon oxide therefrom by the hydrogenation of the carbon oxide to methane under the following conditions:

pressure—atmospheric  
space velocity of the gas—5000/hr<sup>-1</sup>  
catalyst volume 3 cm<sup>3</sup>  
size of the catalyst grains from 1.5 to 2.5 mm

The reagent gas had the following composition (volume %): carbon oxide 0.4, hydrogen 99.6.

The catalyst before testing was reduced at 300°C.

The results of the testing are given in Table XI

TABLE XI  
Residual carbon monoxide  
content in the purified  
gas

| Temperature<br>°C | Residual carbon monoxide<br>content in the purified<br>gas |     |
|-------------------|--|-----|
| 150               | 0.12 vol. %  | 105 |
| 175               | less than 10 ppm   |     |
| 200               | less than 10 ppm   |     |

#### WHAT WE CLAIM IS:—

1. A method of preparing a non-supported catalyst suitable for use in oxidation-reduction reactions, said method comprising providing an aqueous solution or melt of a first component selected from the nitrate and acetate salts of the elements selected from magnesium, aluminium and those of atomic number from 20 to 31 and from 38 to 84, said aqueous solution, if used, having a total salt concentration of from 35 to 80% by weight; obtaining a precursor mass by mixing with the aqueous

5 solution or melt a second component comprising oxalic acid or a powdered compound selected from the carbonates, basic carbonates and hydroxides of the elements selected from magnesium, aluminium and those of atomic number from 20 to 31 and from 38 to 84; and, in the absence of a separate catalyst support, calcining the precursor mass at a temperature within the range from 300 to 700°C.

10 2. A method according to claim 1, wherein the catalyst produced is moulded into tablets.

15 3. A method according to claim 1 or claim 2, in which the precursor mass obtained is vigorously stirred at a temperature within the range from 70 to 100°C, prior to calcining.

20 4. A modification of the method according to any one of claims 1 to 4, in which the first component includes chromium and chromic anhydride is substituted for up to 99.9% of chromium nitrate or acetate calculated as  $\text{Cr}_2\text{O}_3$ , by adding powdered chromic anhydride to the aqueous solution or melt or chromium nitrate before admixture with the second component.

5. A method of preparing a catalyst according to claim 1 and substantially as described hereinbefore.

6. A method of preparing a catalyst substantially as described in any one of the Examples. 30

7. A catalyst for the conversion of carbon monoxide with steam, obtained by the method claimed in any one of claims 1 to 5, comprising:  $\text{CuO}$ —from 30 to 55%;  $\text{MgO}$ —from 25 to 45%;  $\text{Al}_2\text{O}_3$ —from 2 to 30%;  $\text{Cr}_2\text{O}_3$  or  $\text{ZnO}$ —from 0 to 30%, all percentages being by weight. 35

8. A catalyst whenever prepared by the method according to any one of claims 1 to 6. 40

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.